PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2001-053068

(43)Date of publication of application : 23.02.2001

(51)Int.Cl. H01L 21/3065
H01L 21/027

(21)Application number : 2000-174636

(22)Date of filing : 12.06.2000

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(30)Priority

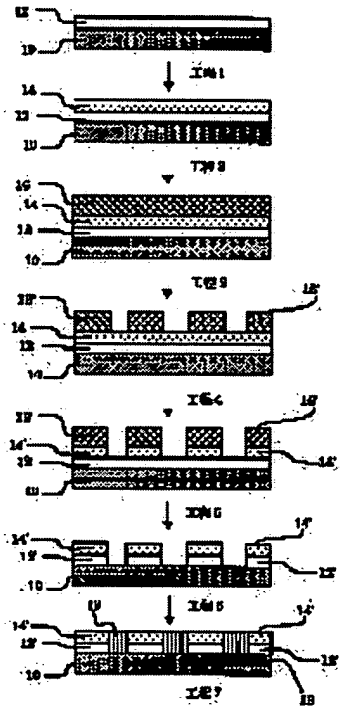
Priority number : 99 330417 Priority date : 11.06.1999 Priority country : US

(54) REFLECTION PREVENTING HARD MASK COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a hard mask improving the resistance of an oxygen base against plasma etching by depositing an organic reflection preventing hard mask composition containing a specified inorganic element on a dielectric layer.

SOLUTION: A reflection preventing hard mask coating layer 14 formed of organic silicon polymer containing the elements of IIIa, IVb, Va, VIa, VIIa, VIII, Ib, IIb, IIIb, IVb and/or Vb groups in a periodic table is applied on a dielectric layer 12. A photoresist coating layer 16 is applied on the reflection preventing hard mask layer 14. The resist layer 16 is exposed, developed and a resist relief image 16' is formed on the reflection preventing hard mask layer 14. Then, the reflection preventing hard mask layer 14 is patterned by a plasma different from the plasma at the time of forming the resist relief image 16' positioned above. Then, a reflection preventing hard mask image 14' matching the resist relief image 16' positioned above is formed.



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[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

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CLAIMS

[Claim(s)]
[Claim 1] (a) Offer an integrated-circuit base which has a dielectric layer on a base.;
(b) Deposit an enveloping layer of an organic acid-resisting hard surface mask blank constituent containing one or more inorganic elements chosen from IIIa, IVa, Va and VIa, VIIa, VIII, Ib and IIb, IIIb, IVb, or Vb group of a periodic table on a dielectric layer.;
(c) Deposit an enveloping layer of a photoresist constituent on an enveloping layer of an acid-resisting hard surface mask blank constituent.;
(d) Expose and develop an enveloping layer of a photoresist constituent with radiation by which pattern attachment was carried out, and form a photoresist relief image on an acid-resisting hard surface mask blank constituent.;
(e) How to form a relief image of this constituent and etch [etches an acid-resisting hard surface mask blank constituent, and] into; pan a dielectric layer located on an integrated circuit or an electro nick packaging substrate including etching a dielectric layer field which carried out (f) exposure.
[Claim 2] An acid-resisting hard surface mask blank constituent is based on total solids of a constituent, and is carbon of about 20 mole percents, and the method according to claim 1 of containing an inorganic atom of about 1 mole percent at least at least.
[Claim 3] A way according to claim 1 an acid-resisting hard surface mask blank constituent has an inorganic atom of about 5 mole percents based on total solids of a constituent.
[Claim 4] A method according to claim 1 chosen from a group which an inorganic atom of an acid-resisting hard surface mask blank constituent becomes from Si, aluminum, and germanium.
[Claim 5] A method according to claim 1 which an acid-resisting hard surface mask blank constituent deposits by spin coating.
[Claim 6] A way according to claim 1 an acid-resisting hard surface mask blank constituent contains a component which has an aromatic series radical.
[Claim 7] A way according to claim 6 an aromatic series radical is a ring type aryl group.
[Claim 8] A method according to claim 6 of being the phenyl group replaced by anthracenyl group by which an aromatic series radical was replaced by arbitration, naphthyl group replaced by arbitration, or arbitration.
[Claim 9] A method containing a component which has a naphthyl group replaced by an anthracene radical or arbitration by which image formation of the photoresist constituent was carried out with radiation with a wavelength of about 248nm, and an acid-resisting hard surface mask blank constituent was replaced by arbitration according to claim 1.
[Claim 10] A method containing a component which has a phenyl group by which image formation of the photoresist constituent was carried out with radiation with a wavelength of about 193nm, and an acid-resisting hard surface mask blank constituent was replaced by arbitration according to claim 1.
[Claim 11] A method according to claim 1 by which a dielectric layer is etched with oxygen content plasma.
[Claim 12] A method according to claim 1 by which an acid-resisting hard surface mask blank

constituent layer is etched with halogen plasma.
[Claim 13] A way according to claim 1 an acid-resisting hard surface mask blank layer is not about 3 time reactivity at least than a dielectric layer to oxygen plasma etching.
[Claim 14] A way according to claim 1 an acid-resisting hard surface mask blank constituent contains a heat acid generator compound.
[Claim 15] A method according to claim 1 hardened thermally [before an acid-resisting hard surface mask blank constituent applies a photoresist constituent layer].
[Claim 16] A method according to claim 1 by which a photo-oxide generating agent is not substantially activated for an acid-resisting hard surface mask blank constituent by exposure of a photoresist constituent layer including a photo-oxide generating agent.
[Claim 17] A way according to claim 1 an acid-resisting hard surface mask blank constituent contains cross linking agent matter.
[Claim 18] (a) Offer a base which has a dielectric layer on a base.;
(b) Deposit at least an enveloping layer of an organic acid-resisting hard surface mask blank constituent which is not reactivity about 3 times rather than a dielectric layer to oxygen plasma etching on a dielectric layer.;
(c) Deposit an enveloping layer of a photoresist constituent on an enveloping layer of an acid-resisting hard surface mask blank constituent.;
(d) Expose and develop an enveloping layer of a photoresist constituent with radiation by which pattern attachment was carried out, and form a photoresist relief image on an acid-resisting hard surface mask blank constituent.;
(e) How to form a relief image of this constituent and etch [etches an acid-resisting hard surface mask blank constituent, and] into; pan a dielectric layer located on an integrated circuit or an electro nick packaging substrate including etching a dielectric layer field which carried out (f) exposure.
[Claim 19] A way according to claim 18 an acid-resisting hard surface mask blank constituent is not about 5 time reactivity at least than a dielectric constituent layer to oxygen plasma.
[Claim 20] A method according to claim 19 by which an acid-resisting hard surface mask blank layer is etched with halogen plasma.
[Claim 21] A base which has a dielectric layer on a base; a covered base containing an enveloping layer of a photoresist constituent on enveloping layer [of an organic acid-resisting hard surface mask blank constituent containing one or more inorganic elements chosen from IIIa, IVa, Va and VIa, VIIa, VIII Ib and IIb, IIIb, IVb, or Vb group of a periodic table on a dielectric layer];, and an enveloping layer of an acid-resisting hard surface mask blank constituent.
[Claim 22] A base which has a dielectric layer on a base; a covered base containing an enveloping layer of a photoresist constituent on enveloping layer [of an organic acid-resisting hard surface mask blank constituent]; on a dielectric layer, and an acid-resisting hard surface mask blank constituent enveloping layer.
[Claim 23] An acid-resisting hard surface mask blank constituent for using it at least based on total solids of a constituent with a photoresist layer containing an organic chromophore which can absorb exposure radiation used for carrying out pattern formation of carbon of about 20 mole percents, and the photoresist layer located in Si of about 1 mole percent, germanium or aluminum atom, and a top by which the overcoat was carried out.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001] This invention relates to the constituent and method for manufacture of an integrated-circuit system. More, the good resistance to the plasma etching of the oxygen base is shown in details, and they are provided with the organic spin-on mold (spin-on type) antireflection film (antireflective coating, ARC) constituent which can serve as a hard surface mask blank (hard mask) in a circuit manufacturing process.
[0002] In manufacture of a semiconductor device, various conductor device fields and layers which were isolated by the dielectric field insulated electrically generally are formed on a device base. These dielectric fields can be manufactured from a silicon dioxide by various technology like oxide growth (oxide growth), sputtering, or other chemical depositing methods, for example. In manufacture of a device, it is required for a dielectric layer to make the opening (opening) which enables the contact and the electric communication link between the fields where devices differ.
[0003] Photolithography is used for forming such a opening in a dielectric layer. The dielectric field which a photoresist has a pattern formed on a dielectric layer, and is exposed after exposure is removed by dry etching and the type target by plasma etching or the ion bombardment (ion bombardment). Refer to U.S. Pat. No. 5468342 and No. 5346586. However, a resist mask is also disassembled and the dielectric layer will be made to reduce the resolution of a ******** image with a pattern, while carrying out plasma etching of the lower layer dielectric matter. Such an imperfect image imprint may spoil the property of a semiconductor device.
[0004] The specific mineral matter known as a hard surface mask blank is inserted between the dielectric and the resist layer, and the imperfection in the image imprint to the dielectric layer located downward from a resist layer is reduced. for example, polish recon, silicon nitride, aluminum, and silicification -- titanium or hard surface mask blank matter like a tungsten is vapor-deposited on a dielectric layer by vacuum deposition like sputtering. Subsequently, image formation of the photoresist is covered and carried out on a hard surface mask blank. The inorganic hard surface mask blank field exposed after the development of a resist is removed by the plasma etching to which an organic resist layer can be equal. The selectivity which was covered an inorganic hard surface mask blank layer and on it, and was comparatively excellent in etching between the resists of the eclipse ******** base with a pattern can be attained. The selectivity of such etching must have been generally produced between a dielectric layer and the resist of the organic substance base. The outline of a hard surface mask blank is in agreement with a resist mask after such etching. The dielectric field exposed after hard surface mask blank etching is alternative to a dielectric next, and a hard surface mask blank can be removed by etching to which can be equal. Since the selectivity which was excellent in etching between the dielectric layer matter and a hard surface mask blank is accepted, the insufficiency [the above images] of an imprint is avoidable. Generally, refer to United States Patent described previously.
[0005] Although such an approach can be effective in manufacture of many integrated circuits, the industrial world is higher resolution, and continues and requires that the further more small structure should be produced. There are other troubles of restricting actually the capacity which forms resolution

and the smaller structure in manufacture of a circuit. For example, an echo of the activity radiation used for exposing a photoresist can restrict the resolution of a ******** image with a pattern in a resist. Especially an echo of the radiation from the interface of a lower layer front face and a photoresist can produce a spatial change of the radiation intensity in the inside of a photoresist, consequently produces the photoresist of uneven line width of face after development. Exposure radiation can also be scattered on the field of the photoresist coat which does not have the intention of exposure, and produces fluctuation of line width of face from the interface of a lower layer front face and a photoresist as a result. Therefore, to have a constituent and a method new for manufacture of an integrated circuit is desired.

[0006] This invention offers the suitable radiation absorptivity constituent of the new organic substance base to use it as an antireflection film constituent (ARC) for the photoresist by which an overcoat is carried out (overcoated). The acid-resisting constituent of this invention can function effectively also as a hard surface mask blank layer by showing sufficient selectivity carrying out plasma etching of the dielectric layer (undercoated) (for example, an inorganic oxide or an organic layer) by which the under coat was carried out, and the photoresist by which the overcoat was carried out. The acid-resisting hard surface mask blank constituent of this invention contains the component replaced with the inorganic substance which can offer the selectivity of etching. For example, the desirable acid-resisting hard surface mask blank constituent of this invention contains in one or more inorganic elements and a type target the element of IIIa of a periodic table, IVa, Va and VIa, VIIa, VIII, Ib and IIb, IIIb, IVb, and/or Vb group, and 1 or more [of the component which contains silicon, germanium, and aluminum especially more preferably]. For example, the acid-resisting hard surface mask blank constituent of this invention can contain organic silicon polymer like the copolymer offered by the reaction of the acrylic monomer which has a substituent containing Si.

[0007] The acid-resisting hard surface mask blank constituent of this invention also contains the chromophore component which can absorb effectively the exposure radiation used for carrying out pattern attachment of the resist (overlying) layer located upwards preferably. A chromophore is changeable according to the exposure wavelength used for the photoresist by which an overcoat is carried out. For example, about the resist by which image formation is carried out by 248nm, an acid-resisting hard surface mask blank constituent can contain suitably the resin or other components which have an anthracene or a naphthyl group. For example, about the resist by which image formation is carried out by 193nm, an acid-resisting hard surface mask blank constituent can contain suitably the resin or other components which have a phenyl group. Single resin can also contain an absorption-of-radiation nature chromophore and the inorganic radical which can offer the selectivity of etching. Between processings, preferably, an acid-resisting hard constituent is hardened and a bridge is constructed over it.

[0008] This invention also includes the method for carrying out pattern attachment of the electro nick packaging devices (electronic packaging device), such as a base, especially a semiconductor wafer, and processing them. More, the desirable method of this invention provides details with the base (for example, semiconductor wafer) which has a dielectric surface layer, and includes applying the enveloping layer of the acid-resisting hard surface mask blank constituent of this invention on it in them. The organic acid-resisting hard surface mask blank constituent is more more convenient than the typical vacuum evaporationo which can be applied by spin coating and used for application of the present inorganic hard surface mask blank layer clearly.

[0009] Subsequently, a photoresist layer is applied on an acid-resisting hard surface mask blank layer, and with the radiation by which pattern attachment was carried out, image formation of the resist layer is carried out, it is developed, and offers a relief image on an acid-resisting layer. subsequently, the selectivity of etching [image / to which the overcoat of the acid-resisting hard surface mask blank was carried out / resist relief] of reactivity, for example, an acid-resisting hard surface mask blank layer:photoresist relief image, by the acid-resisting layer -- at least -- about 3:1 -- it is more preferably etched further more at least preferably with about 5:1 and the plasma which is about 7:1 or 10:1 at least. For example, the acid-resisting hard surface mask blank layer containing a silicon mineral constituent

can be selectively etched with the plasma of the fluorine base. The acid-resisting hard surface mask blank layer containing aluminum mineral constituent can be selectively etched with the plasma of the chlorine base.

[0010] The etching processing offers the relief image of the acid-resisting hard surface mask blank constituent which is in agreement with the relief image of a resist which is located upwards, and by which pattern attachment was carried out. Subsequently, the dielectric layer to which reactivity with an acid-resisting hard-surface-mask-blank layer is low, for example, as for the field of the exposed dielectric layer, is located downward relatively (underlying): The etch selectivity which is an acid-resisting hard surface mask blank layer is preferably etched by about 5:1 pan at least at least more preferably with about 3:1 and the plasma which is about 7:1 or 10:1 at least. For example, a dielectric layer of Si base like the layer of silicon nitride or silicon oxide could be selectively etched with the suitable halogen plasma, and the organic dielectric layer was able to be selectively etched with the plasma of the oxygen base. Subsequently the field of the base exposed after such etching of a dielectric layer is selectively processible into appearance like metalization desired.

[0011] If the mode of this invention is illustrated more concretely, the acid-resisting hard surface mask blank matter containing Si can be etched with halogen plasma like a fluorine or the chlorine plasma, and the organic dielectric layer located downward can be selectively etched with the plasma of the oxygen base. In other modes, the acid-resisting hard surface mask blank matter containing aluminum can be etched with the plasma of the chlorine base, and SiO2 dielectric layer located downward can be selectively etched with the plasma of the fluorine base. This invention offers the new industrial product containing a base like the micro electro nick wafer covered combining the dielectric layer located in the photoresist constituent by which is acid-resisting hard surface mask blank constituent independent [of this invention], or the overcoat was carried out further, and/or the bottom. Other modes of this invention are indicated below.

[0012] As mentioned above, this invention offers the new acid-resisting hard surface mask blank constituent which can be applied as a spin-on compound. The constituent of this invention can show the good selectivity of etching to the dielectric layer located in the bottom like SiO2, mineral matter like other inorganic oxides, or an organic resin layer. An acid-resisting hard surface mask blank constituent is the mixture of an inorganic element like a carbon radical (carbon groop) and Si and As, and/or germanium. here, it means with that with which an inorganic atom or an element puts not carbon but hydrogen, nitrogen, oxygen, or polyads other than sulfur -- having -- desirable -- the element of IIb of a periodic table, IIIb, IVb and Vb, or a VIb group -- it is the element of the group of IIIb of a periodic table, or IVb more preferably.

[0013] Probably, the acid-resisting hard surface mask blank constituent contains about 3 or the inorganic element of 5 mole percents for the inorganic element of at least 1 mole percent at least typically based on the total solids (all components except a solvent carrier) of a constituent based on the total solids (all components except a solvent carrier) of a constituent. Probably, the acid-resisting hard surface mask blank constituent contains about 7, 10 and 12, or the inorganic element of 15 mole percents at least more preferably based on the total solids of a constituent. For example, probably, more inorganic contents which contain about 17, 20, 25, 30 and 35, or the inorganic element of 40 mole percents at least based on the total solids of a constituent will also be suitable for an acid-resisting hard surface mask blank constituent. The acid-resisting hard surface mask blank constituent has the substantial carbon content typically, for example, about 10, 15, or 20 mole percents are carbon even if there are few constituents based on total solids. More preferably, about 25, 30, 35, 40 and 50, or 60 mole percents are carbon, even if there are few constituents based on total solids. One or more [of the chromophore which absorbs the exposure radiation of the photoresist by which the overcoat was carried out] is the above aromatic series carbon radicals typically.

[0014] Especially in drawing 1 by which the desirable method of this invention is generalized and illustrated, in a process 1, a base 10 has the dielectric layer 12 by which the overcoat was carried out, and is offered. Bases 10 can be electro nick packaging devices, such as for example, a semiconductor wafer and a microchip module. For example, a base 10 can be the micro electro nick wafer of silicon, a

silicon dioxide, aluminum, or an aluminum oxide. As other bases which can be used, the base of gallium arsenide, gallium nitride, the indium base, a ceramic, a quartz, or copper is mentioned.
[0015] A layer 12 can be matter of various classes used for the structure which isolates an inorganic oxide like SiO2, parylene (parylene), a resin layer like fluorination ANHO lath carbon (fluorinated amphorous carbon), or the processed base 10, and is insulated electrically. In the process 2 of drawing 1 , the enveloping layer 14 of the organic acid-resisting hard surface mask blank constituent of this invention is applied on a layer 12. An enveloping layer 14 can be applied by carrying out spin coating of the coat nature compound of a liquid on a layer 12, then clearance of a solvent carrier can be made by the vacuum hot plate for 60 seconds at about 90 degrees C. An acid-resisting hard surface mask blank constituent is generally applied to about 0.02-0.5-micrometer desiccation thickness and a twist type target on a base by about 0.04-0.20-micrometer desiccation thickness.
[0016] As mentioned above, the coat of an acid-resisting hard surface mask blank constituent contains the chromophore portion for the absorption of the exposure radiation of a photoresist layer by which the overcoat was carried out, and the component which has the inorganic radical which offers the selectivity of the plasma etching to the dielectric layer 12 arranged downward. The desirable acid-resisting hard surface mask blank constituent of this invention contains the constituent containing the resin which has a chromophore and/or an inorganic radical on resin. Resin is the organic substance preferably. For example, the polymer which has [which is] pendant chromophore radicals, such as anthracenyl (as opposed to 248nm), phenyl (as opposed to 193nm), and naphthylene, like ring type aryl or a hetero aromatic series radical for effective absorption of exposure radiation can be used. The resin containing a desirable chromophore and a desirable chromophore is Shipley. It is indicated by U.S. Pat. No. 5851730 and the Europe patent disclosure official report 813114ANo. 2 which were transferred to Company.
[0017] The resin which has both a chromophore and the inorganic radical of etching-proof nature can be easily prepared by reaction of suitable monomer mixture like the reaction of the monomer which has inorganic etching-proof nature elements (for example, Si, germanium, aluminum, etc.), and the monomer which has a desired chromophore radical. Such a monomer is commercially available and can be compounded easily. For example, the acrylic monomer which has Si radical can come to hand from the sale company of many, such as Gelest and Inc. (Tullytown, PA). As a typical monomer, a meta-acrylic oxymethyl tris-(trimethylsiloxy) silane, an allyl compound tris (trimethylsiloxy) silane, allyl compound trimethoxysilane, a vinyl tris (trimethylsiloxy) silane, vinyltrimetoxysilane, vinyl (3, 3, and 3-trifluoro propyl) dimethylsilane, vinyl triphenoxysilane, a vinyl triethyl silane, vinyltriacetoxysilane, etc. are mentioned more preferably. Vinyl end silicon polymer like p-dimethylsiloxane of a vinyl end or a meta-acrylic oxy-propyl end is usable, and it is heated until it can be included in other polymer by suitable reaction like the free radical polymerization under existence of an initiator like 2 and 2' azobis isobutyl nitril and a reaction is typically completed under a desirable existence of suitable solvents, such as a tetrahydrofuran, by it. Refer to the following examples 1 for the typical synthesis method of the acid-resisting hard surface mask blank constituent of this invention.
[0018] By the same method, other mineral matter is incorporable into the component of the acid-resisting hard surface mask blank constituent for using it according to this invention. For example, the monomer which has the inorganic atom of one or more requests and in which other polymerizations are possible can react, and resin can be formed. Such a monomer is commercially available from sale companies, such as Gelest and Inc. For example, as a suitable monomer, allyl compound triethyl germane, allyl compound trimethyl germane, METAAKURIRU oxy-triethyl germane, tetra-allyl compound germane, vinyl triethyl germane, etc. can be mentioned. The suitable aluminum matter is also commercially available.
[0019] Furthermore, an inorganic etching-proof nature component and an inorganic acid-resisting component can be the blended matter separate from the acid-resisting hard surface mask blank constituent of this invention. For example, the polymer which has a mineral constituent can be blended with the organic polymer containing an exposure absorption-of-radiation nature chromophore. For example, as an example of suitable inorganic etching-proof nature polymer, a silicon content is high and alcoholic end copolymer [of the carbinol functionality copolymer; dimethylsiloxane and ethylene oxide

of a SHIRISESUKI oxane; epoxy propoxy propyl end p-dimethylsiloxane; methyl siloxane and dimethylsiloxane like p-methyl SHIRISESUKI oxane with a lower silanol content]; and silanol end p-dimethylsiloxane is mentioned. An inorganic cross linking agent can also be used. For example, aluminum s-butoxide An aluminum cross linking agent like a screw (ethyl acetoacetate) can be suitable to provide an acid-resisting hard surface mask blank constituent with a desired mineral constituent content. The polymer of the typical organic substance base which has a chromophore which can be blended with such polymer is indicated by U.S. Pat. No. 5851730 of Shipley, and the Europe patent disclosure official report 813114ANo. 2. Suitable phenyl content polymer is Shipley to 193nm resist image formation. It applies on September 15, 1998 transferred to Company, and is indicated by the United States Patent application 09th which is pending in court / No. 153575. Especially the application consists of a radical to which the polymerization of styrene, 2-hydroxyethyl methacrylate, and the methylmetaacrylate was carried out, and indicates the desirable acid-resisting terpolymer each mole ratio of whose is 30:38:32.

[0020] In addition to the inorganic element and inorganic chromophore unit of etching-proof nature, the polymer of the acid-resisting hard surface mask blank constituent of this invention can include other units. For example, an alicyclic-in resin of constituent of this invention radical, such as pendant cyano group; itaconic-acid-anhydride radical; adamanthyl, norbornyl, and cyclohexyl; it can have ring type aryl group; like naphthyl and a phenol etc.

[0021] Preferably, the resin of a constituent or all the molar quantity of oligomer are amounts of about 3, 4, 5, 6 and 7, or 8 mole percents at least, and the mixed resin or the oligomer component of an acid-resisting hard surface mask blank constituent of this invention has one or more inorganic etching-proof nature components. The inorganic etching-proof nature atom of more amounts can be used, for example, it is the concentration of about 10, 12 and 15, or the inorganic etching-proof nature element of 20 mole percents at least based on the resin of a constituent, or the whole quantity of oligomer. As mentioned above, the resin or the oligomer component which contains an acid-resisting chromophore and an inorganic etching-proof nature element as a component of the typical acid-resisting hard surface mask blank constituent of this invention; when a bridge formation component exists, the source of an acid, cross linking agent;, and a solvent carrier are mentioned typically. However, a constituent can contain an additional component. For example, the element of an acid-resisting chromophore and inorganic etching-proof nature can be offered with the low-molecular (for example, molecular weight smaller than about 500) additive of non-polymer nature.

[0022] The molecular weight of the resin of the acid-resisting hard surface mask blank constituent of this invention can change comparatively broadly, for example, can be weight average molecular weight (Mw) which is about 1,000 - 1,000,000dalton of abbreviation. The acid-resisting chromophore of the constituent of this invention and the concentration of an inorganic etching-proof nature component can change comparatively broadly, and generally, these components are used by the concentration of about 50 to 95 percentage by weight of the weight of all the desiccation components of a constituent, and, more typically, are about 60 to 90 percentage by weight of all desiccation components (all components except a solvent carrier).

[0023] The acid-resisting hard surface mask blank constituent of the bridge formation mold of this invention also contains a cross linking agent component or the matter. the glycouril (glycouril) cross linking agent which various cross linking agents can be used and is indicated by U.S. Pat. No. 5851730 of above-mentioned Shipley -- especially -- from an American cyanamide company -- commercial -- an available trade name -- Powderlink An ARC cross linking agent like the methoxymethyl-ized glycouril which is 1174 is included. The cross linking agent of other amine bases can be suitable. For example, a melamine cross linking agent, especially Cymel The melamine-formaldehyde resin sold as a trade name Cymel by American cyanamide company like 300, 301, 303, and 350 can be suitable. By the American cyanamide company, it is Bettle. It is Cymel by the urea-resin sold as 60, 65, and 80, and the American cyanamide company. Resin of the benzoguanamine base like the benzoguanamine resin sold by the trade name of 1123 and 1125 and the resin of the urea base can also be suitable.

[0024] Since the catalyst of the reaction of a cross linking agent while hardening an acid-resisting hard

surface mask blank enveloping layer is carried out or preferably promotes it, the cross-linking acid-resisting hard surface mask blank constituent of this invention contains an acid or an acid generator compound further. Preferably, the acid generator compound which separates an acid by the photolysis or heat treatment is used. Preferably, as an acid generator, a heat acid generator, i.e., the compound which generates an acid after heat treatment, is used. For example, various well-known heat acid generators like benzoin tosylate, nitrobenzyl tosylate (especially 4-nitrobenzyl tosylate), and the alkyl ester of other organic sulfonic acids are used suitably. A desirable heat acid generator is King. Nacure which can come to hand from Industries It is 5225. After activation, the compound made to generate a sulfonic acid is suitable generally. Typically, a heat acid generator exists in a cross-linking acid-resisting hard surface mask blank constituent by the concentration of about 0.3 to 3 percentage by weight of all the desiccation components of a constituent. In addition to the heat acid generator instead of a heat acid generator, a photo-oxide generating agent can be used as an acid generator, and the field of an acid-resisting hard surface mask blank enveloping layer is exposed to activity radiation before application of the photoresist constituent by which an overcoat is carried out.

[0025] It is not an acid generator but the acid-resisting hard surface mask blank constituent which needs heat for an acid also only being blended with the cross-linking acid-resisting hard surface mask blank constituent of this invention, and hardening under existence of an acid especially, and before the activity of a constituent, since an acid does not promote the reaction the component of a constituent is not wished, it can be blended with a case. as a suitable acid -- the sulfonic acids like toluenesulfonic acid and a sulfonic acid for example, and triflic one -- the mixture of acid (triflic acid) or these matter is mentioned.

[0026] This invention also contains the acid-resisting hard surface mask blank constituent which does not construct a bridge intentionally between the activities with a photoresist constituent meant. Such a non-cross-linking constituent does not need the cross linking agent component, acid, or heat acid generator for guiding or promoting crosslinking reaction. or [that in other words such a non-cross-linking acid-resisting hard surface mask blank constituent does not have the source of the cross linking agent component and/or acid for promoting crosslinking reaction in essence typically] (for example, about 1 or less than 2 % of the weight) -- or it does not have thoroughly.

[0027] When the process 2 of drawing 1 is referred to again and an acid-resisting hard surface mask blank constituent is a constituent of cross-linking, preferably, before application of a photoresist layer, a constituent is this process and is hardened selectively at least. Heat treatment is desirable generally. Hardening or bridge formation conditions will change according to the component of an acid-resisting hard surface mask blank constituent. Heating the base 10 covered with about 200 degrees C for about 10 - 30 minutes as suitable conditions, for example is mentioned.

[0028] The acid-resisting constituent of this invention is desirable, and also including one or more photo-oxide generating agents (PAG), it is sufficient amount to forbid notching (notching) or the footing (footing) which is not expected the photoresist layer by which the overcoat was carried out, or bar substantially, and is used suitably. In this mode of this invention, a photo-oxide generating agent is not used as the source of the acid for promoting crosslinking reaction, and, therefore, a photo-oxide generating agent is not preferably activated substantially during bridge formation of an acid-resisting constituent (in the case of a cross-linking acid-resisting hard surface mask blank constituent). About the case of the acid-resisting hard surface mask blank constituent over which a bridge is especially constructed with heat, in the case of exposure of the resist layer to which PAG of an acid-resisting hard surface mask blank constituent is substantially stable to the conditions of crosslinking reaction, and the overcoat of the PAG was carried out after that, it is activated and an acid is made to be generated. especially desirable PAG -- the temperature of about 140 degrees C or 150 degrees C - 190 degrees C -- it is -- 5 minutes - 30 minutes or more than it -- even if it carries out time amount exposure, dissociation or decomposition of other modes is not carried out substantially, either. Such PAG in an antireflection film constituent and its activity are Shipley. It is indicated by the United States Patent application number 08th for which it applied on February 6, 1997 / No. 797741 and the response Japan disclosure patent official report by Pavelchek and others which were transferred to Company, and the publication

number No. 61845 [ten to]. Suitable PAG to use it for the acid-resisting hard surface mask blank constituent of this invention is clarified by the following description of Photoresist PAG. as the desirable photo-oxide generating agent for such an activity [in / generally / ARC of this invention] -- onium salt [like JI (4-tert-buthylphenyl) iodonium perfluoro octane sulfonate for example,] and 1, and 1-screw [p-chlorophenyl] - a halogenated nonionic photo-oxide generating agent like 2, 2, and 2-trichloroethane is mentioned.

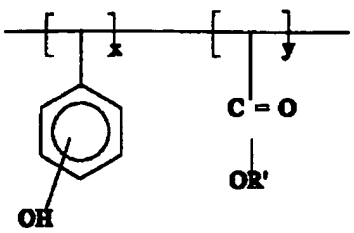
[0029] The acid-resisting hard surface mask blank constituent of this invention can also contain the additional color compound which absorbs the radiation used for exposing the photoresist layer by which an overcoat is carried out. As an additive of other arbitration, it is the trade name Silwet which can come to hand from Union Carbide, for example. A surface lubricating agent like the lubricating agent of 7604 or the surfactant FC430 which can come to hand from 3M company is mentioned. A desirable surfactant is the concentration of 0.2 - 1.5% of solid content.

[0030] In order to manufacture the liquid coat nature acid-resisting hard surface mask blank constituent suitable for spin-on application, the component of a constituent For example, ethyllactate;2-methoxy ethyl ether (jig lime), One or more [of ethylene glycol monomethyl ether and glycol ether like propylene glycol monomethyl ether]; Methoxybutanol, The solvent which has both the ether like an ethoxy butanol, methoxy propanol, and ethoxy propanol, and a hydroxy portion; Methyl-cellosolve acetate, Ethylcellosolve acetate, propylene-glycol-monomethyl-ether acetate, It dissolves in a suitable solvent like other solvents including ester; and 2 base ester like dipropylene-glycol-monomethyl-ether acetate, propylene carbonate, and a gamma-butyrolactone. It depends for the concentration of the desiccation component in a solvent on some factors [like] which are the application method. Generally, the solid content content of an acid-resisting hard surface mask blank constituent changes in the range of about 0.5 to 20 percentage by weight of the AUW of an acid-resisting hard surface mask blank constituent, and a solid content content changes preferably in the range of about two to 10 percentage by weight of the AUW of a constituent.

[0031] Next, according to the process 3 of drawing 1 , the photoresist enveloping layer 16 is applied on the acid-resisting hard surface mask blank layer 14. On the occasion of application of a layer 14, a resist can be applied with the means of the standard of arbitration like spinning. Various photoresist constituents including a positive type and a negative-mold photo-oxide generating agent constituent can be used for the acid-resisting hard surface mask blank constituent of this invention. The photoresist for using it with ARC of this invention contains a photo-oxide generating agent compound in a resin binder, and an optical active ingredient and a type target generally. Preferably, a photoresist resin binder has a functional group and it gives the development possibility by the alkaline water to the resist constituent by which image formation was carried out. Generally, especially the desirable photoresist for using it with the acid-resisting constituent of this invention is a chemistry amplification mold resist of a positive type and a negative mold. many chemistry amplification mold resist constituents -- for example, U.S. Pat. No. 4968581; -- it is indicated by; of; of 4883740 No. 4810613 No. No. 4491628, and No. 5492793, and these instruction about manufacture and an activity of all these chemistry amplification positives resist is referred to as some of these descriptions. Especially a desirable chemistry amplification mold photoresist becomes an activity with the acid-resisting constituent of this invention from the mixture of the resin binder containing the copolymer which has both a photo-oxide generating agent, phenol nature, and a non-phenol nature unit. For example, one of the desirable radicals of such a copolymer has an acid lei building radical (acid labile groups) only on the non-phenol nature unit of a copolymer intrinsically or thoroughly substantially. Especially one of the desirable copolymer binders has the repeat unit of x and y of a degree type.

[0032]

[Formula 1]



[0033] the inside of a formula, and the copolymer whole -- setting -- hydroxyl -- or [any of alt.** meta or the para position] -- existing -- R' -- 1- about 18 carbon atoms -- more -- typical -- 1- it is the substitute or the unsubstituted alkyl which has about 6-8 carbon atoms. tert-butyl is desirable R' radical generally. R' radical can be replaced by arbitration by one or more [, such as a halogen (especially F, Cl, or Br) and two to C1-8 alkoxy **C8 alkenyl,]. Unit x and y can be alternations regularly in a copolymer, or the whole polymer can be dotted with them at random. Such a copolymer can be formed easily. For example, substitute or unsubstituted alkyl acrylate, such as a vinyl phenol and t-butyl acrylate, can condense under well-known free radical conditions for the resin of an above-mentioned formula. The R'-O-C(=O)-portion of a substitute ester portion, i.e., an acrylate unit, will work as an acid lei building radical of resin, and cutting guided to photo-oxide after exposure of the enveloping layer of the photoresist containing resin will be received. desirable -- a copolymer -- about 8000- about 50000 -- more -- desirable -- about 15000 - about 30000 Mw -- having -- about three or less molecular weight distribution -- it has about two or less molecular weight distribution more preferably. A copolymer with a vinyl alicyclic compound like alkyl acrylate, vinyl norbornyl, or a vinyl cyclohexanol compound like non-phenol nature resin, for example, t-butyl acrylate, or t-butyl methacrylate can also be used as a resin binder in the constituent of this invention. Such a copolymer can also be manufactured by such free radical polymerization or other well-known methods, and, probably, has about 8000 - about 50000 Mw, and about three or less molecular weight distribution appropriately. It is indicated by U.S. Pat. No. 5700624 [of Sinta's and others U.S. Pat. No. 5258257;Thackeray and others];, and Barclay's and others U.S. Pat. No. 5861231 as another desirable chemistry amplification positive type resin.

[0034] When a negative-resist constituent desirable although it is used with the acid-resisting constituent of this invention is exposed to an acid, it contains the matter which will be hardened, and will be constructed for which a bridge or solidified, and the mixture of a photo-oxide generating agent. Especially a desirable negative-resist constituent contains a resin binder like phenol nature resin, a cross linking agent component, and the optical active ingredient of this invention. Such a constituent and its activity are indicated by the Europe patent disclosure official report No. 0164248, No. 0232972, and Tackeray's and others U.S. Pat. No. 5128232 number. As desirable phenol nature resin, a novolak and above Pori (vinyl phenol) are mentioned to using it as a resin binder component. As a desirable cross linking agent, the matter of the matter of the amine base containing a melamine, glycouril, and the benzoguanamine base and the matter of the urea base are mentioned. Melamine-formaldehyde resin is the most desirable generally. Such a cross linking agent is commercially available, for example, melamine resin is a trade name Cymel from an American cyanamide company. It is sold as 300, 301, and 303. Glycouril resin is a trade name Cymel from an American cyanamide company. 1170, 1171, 1172, Powderlink It is sold as 1174, the resin of the urea base is sold as a trade name 60, 65, and Beetle 80, and benzoguanamine resin is a trade name Cymel further. It is sold as 1123 and 1125.

[0035] Nonionic organic light activity compounds including the sulfonate photo-oxide generating agent which contains onium salt (the publication of those reference is referred to as some of these descriptions); which is indicated by U.S. Pat. No. 4442197, No. 4603101, and No. 4624912, a halogenation light activity compound [as / in Thackeray's and others U.S. Pat. No. 5128232], sulfonation ester, and sulfonyl oxyketone as a suitable photo-oxide generating compound of the resist used with the acid-resisting hard surface mask blank constituent of this invention are mentioned. Benzoin tosylate, t-buthylphenyl Alpha (p-toluenesulfonyloxy)-acetate and t-butyl J.of for the disclosure containing alpha (p-toluenesulfonyloxy)-acetate of suitable sulfonate PAG Photopolymer Science and Refer to Technology and 4(3):337-340 (1991). Desirable sulfonate PAG is indicated by Sinta's and

others U.S. Pat. No. 5344742. It is a photo-oxide generating agent desirable to the resist constituent with which the camphor sulfonate PAG of the formulas I and II of the column 6 of U.S. Pat. No. 5879856 is used with the acid-resisting constituent of this invention, especially the chemistry amplification mold resin of this invention.

[0036] In the process 3 of drawing 1 , as for a photoresist enveloping layer, a solvent is removed after application of the above resist layers 16 until it dries with heat and a resist layer becomes a tuck free-lancer preferably typically. In the case of being the optimal, mixing between the layers of an ARC layer and a photoresist layer does not take place in essence.

[0037] Subsequently, a resist layer is a well-known method and image formation is carried out with activity radiation through a mask. Exposure energy is enough to produce the image the optical active ingredient of a resist system was activated effectively, and pattern formation was carried out [image] to the resist enveloping layer, and, more specifically, typically, exposure energy is the range of about three to 300 mJ/cm2 according to an exposure means. In a request, the exposed resist layer can be applied at BEKU after exposure, and can produce the soluble difference between the exposure field of an enveloping layer, and a non-exposing field, or can be increased. For example, in order that a negative-mold acid hardenability photoresist may trigger typically the crosslinking reaction promoted from an acid, heating after exposure is needed, and many chemistry amplification positives resist need heating after exposure, in order to trigger the deprotection (deprotection) reaction promoted from an acid. Typically, the conditions of BEKU after exposure are more specifically the temperature of the range of about 50 degrees C - 160 degrees including the temperature of about 50 degrees C or more. Image formation of the resist can be carried out with wide range exposure energy, for example, I-line exposure (365nm), deep UV, wavelength like 248nm, 193nm shorter than 200nm, and 157nm, e-beam, EUV, ion projection lithography (ion projection lithography, IPL), X-line, and ultrashort-wave length that is shorter than other 20nm are mentioned especially.

[0038] After a latent image is formed in a resist layer, a resist is developed in step 4 of drawing 1 (that is, the field exposed when it was a positive resist is removed, and the field which is not exposed is removed when it is negative resist). Wet development is suitable, for example, as shown in the process 4 of drawing 1 using an aquosity tetrabutylammonium hydroxide solution or other aquosity alkaline solutions, resist relief image 16' is offered on the acid-resisting hard surface mask blank layer 14. In a request, a photoresist layer can also be developed by dry type using the plasma (for example, plasma of the oxygen base).

[0039] In a process 5, pattern attachment of the acid-resisting hard surface mask blank layer 14 is carried out with the plasma used for forming resist relief image 16' located upwards, and different plasma. for example, -- acid resisting -- a hard surface mask blank -- a layer -- a fluorine -- or -- chlorine -- the base -- the plasma -- like -- a halogen -- the base -- the plasma -- etching -- having -- drawing 1 -- a process -- five -- being shown -- having -- as -- a top -- being located -- a resist -- relief -- an image -- 16 -- ' -- being in agreement -- acid resisting -- a hard surface mask blank -- relief -- an image -- 14 -- ' -- it can provide . Especially the matter desirable although the acid-resisting hard surface mask blank layer containing Si is etched is plasma formed in the gas flow of CF3, and does not contain oxygen substantially preferably (fewer than 3 or five-mol %). Especially the plasma etching agent of the chlorine base etches the acid-resisting hard surface mask blank layer containing aluminum.

[0040] Then, as shown in the process 6 of drawing 1 , it is etched by the plasma of for example, the oxygen base, and as for the plasma, the dielectric layer 12 located downward can remove the dielectric layer 12 by which a mask is not carried out by resist relief image 16' and acid-resisting hard surface mask blank layer 14' by which pattern formation was carried out, and bears acid-resisting hard surface mask blank layer 14' as mentioned above at the plasma of the oxygen base for the mineral constituent of layer 14'.

[0041] Subsequently, the field which the front face of the base 10 demarcated selectively could be processed like a request, for example, was demarcated is metalized by vacuum evaporationo of copper, aluminum, a tungsten, other conductive metals, or these alloys, and can offer circuit trace or erection RIKARUINTA KONEKUTOBAIA 19 which is illustrated by the process 7 of drawing 1 . A metal

desirable although Bahia or trace 19 is formed is CVD copper or electroplating copper. The publication of all the reference quoted here is referred to as some of these descriptions. The following un-limiting-example illustrates invention.

[0042] Composition of the organic silicon polymer of example 1 this invention.

15.00g 9-anthracene methylmetaacrylate, 5.61g 2-hydroxyethyl methacrylate, and 26.33g 3 [tris (trimethylsilyloxy) silyl] propyl methacrylate were dissolved in the tetrahydrofuran which is 320g. The indirect desulfurization gas of the solution was carried out by the stream of desiccation nitrogen for 10 minutes, and it was heated by 45 degrees C. Subsequently, 0.475g polymerization initiator, 2, and 2' azobis isobutyl nitril was added by the solution, and the solution was heated under reflux for 24 hours. The vacuum drying of the polymer product was collected and carried out by precipitating in the deionized water of 12L. Yield was 84%. Weight average molecular weight (as opposed to a polystyrene standard) was 22,000.

[0043] Preparation and an activity of the constituent of example 2 this invention.

ARC / hard surface mask blank constituent of this invention are the organic silicon polymer (10g) of the above-mentioned example 1, and Powderlink. A 1174 glycouril cross linking agent (1.5g) and Para-toluenesulfonic acid (0.2g) were mixed in the solvent of ethyllactate, and it was prepared by considering as the compound of about 4 % of the weight of the total solid content. The spin coat of its ARC / the hard surface mask blank constituent was carried out on the hardened dielectric layer (epoxy layer), it dried and it offered the enveloping layer with a thickness of about 100nm. Subsequently, the spin coat of the available positive type photoresist was commercially carried out on the ARC layer, the layer with a thickness of about 300nm was formed, and the resist layer was exposed by eclipse ******** with a pattern with a wavelength of 248nm, was developed with the aquosity alkalinity developer, and offered the resist relief image. Subsequently, pattern attachment of ARC / the hard surface mask blank layer was carried out with the fluorine plasma, and it was etched after that with the oxygen plasma in which a lower layer dielectric layer does not contain a fluorine.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] Drawing 1 is drawing showing the desirable mode of the method of this invention.
[Description of Notations]
10 Base
12 Dielectric Layer
12' dielectric relief image
14 Enveloping Layer of Organic Acid-Resisting Hard Surface Mask Blank Constituent
14' organic acid-resisting hard surface mask blank relief image
16 Photoresist Enveloping Layer
16' resist relief image
19 Bahia or Trace

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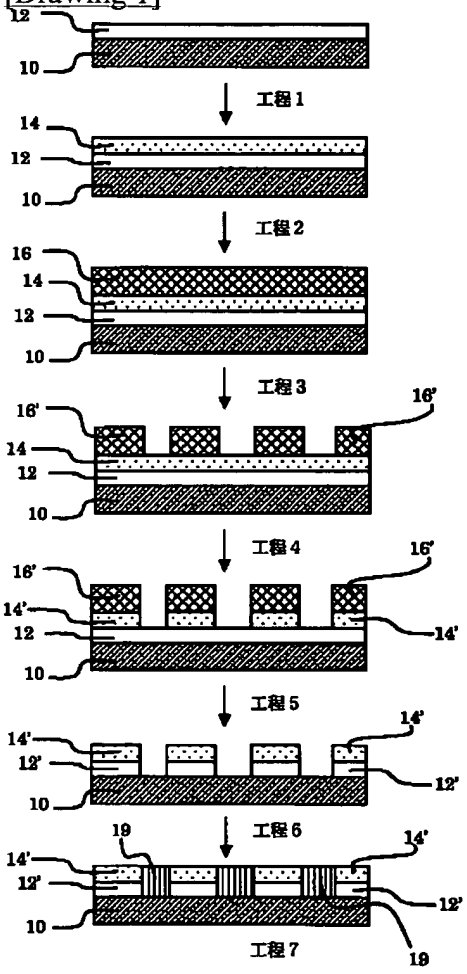
DRAWINGS

[Drawing 1]



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